Ionization potentials within semiempirical APSLG approach.

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Abstract

The APSLG-MINDO/3 method is evolved to reproduce the vertical ionization potentials for organic molecules. Two different schemes — one allowing for adjustment of the local electronic structure to the hole in each configuration and another one with a fixed local electronic structure — are developed and implemented. These methods are applied to a series of normal hydrocarbons. The possibility of localization of a hole in the polyethylene cation is discussed. Vertical ionization potentials are also obtained for a set of organic molecules with heteroatoms. Their values together with degeneracy of ionized states are compared with the data of photoelectron spectroscopy.

1 Introduction

The calculations of the vertical ionization potentials are usually performed on the basis of the Hartree-Fock approximation. Most workers in the field of photoelectron spectroscopy use the one-electron approximation and the Koopmans' theorem [?] as primary tools allowing to estimate the vertical ionization potentials. There exist also elaborated methods of the calculation of vertical ionization potentials employing the configuration interaction or perturbation expansions. The success of the Hartree-Fock based methods in explaining degeneracies of the energy eigenstates have led to a widely spread point of view that the observed form of the photoelectron spectra confirms the orbital structure and the one-electron character of the molecular electronic wave functions. Thus it is interesting to explore the methods of the calculation of ionization potentials which do not rely upon the one-electron picture mentioned above. It is also important to investigate a capacity of a method based on the local description of molecular electronic structure to describe the ionic states and to reproduce their symmetry properties ultimately interpreted as delocalization. Some attempts in this direction were made in Refs. [?, ?].

Our previous work [?, ?] was devoted to development of semiempirical quantum chemical method, using the trial wave function of electrons taken as the antisymmetrized product of strictly localized geminals (APSLG) [?, ?, ?]. Starting from the MINDO/3 Hamiltonian we modified its resonance parameters and obtained the computational scheme which turned out to be more efficient than the original MINDO/3 method based on the self-consistent field (SCF) approximation. The present work is devoted to extension of the APSLG-MINDO/3 approximation [?, ?] towards calculation of ionization potentials.

Now we briefly remind the main features of the semiempirical APSLG-MINDO/3 approach [?, ?]. Within this approach the basis set of AO's is replaced by that of the hybrid orbitals (HO's). The transition to the local description is carried out by the unitary transformation (with optimized parameters of the latter) on each "heavy" (non-hydrogen) atom. Each HO is assigned to a chemical bond or an electron lone pair. Therefore, each (m-th) chemical bond is expanded through two HO's — $|r_m\rangle$ and $|l_m\rangle$ (right and left). The wave function of the APSLG type is constructed as antisymmetrized product of the geminals — two-electron functions. In the second quantization language it can be written as:

$$|\Phi\rangle = \prod_m g_m^+ |0\rangle \, . \tag{1}$$

Each geminal can be presented as a sum of three singlet two-electron configurations in the basis of four spin-orbitals assigned to this chemical bond:

$$g_m^+ = u_m r_{m\alpha}^+ r_{m\beta}^+ + v_m l_{m\alpha}^+ l_{m\beta}^+ + w_m \left(r_{m\alpha}^+ l_{m\beta}^+ + l_{m\alpha}^+ r_{m\beta}^+ \right) \tag{2}$$

with variable amplitudes u_m, v_m, w_m. The first and the second terms correspond to the ionic configurations with two electrons on the same (the right or the left respectively) end of the chemical bond. The third term represents the covalent contribution to the geminal, *i.e.* it is analogous to the Heitler-London wave function of the dihydrogen molecule [?]. In the case of the electron lone pairs only one of the ionic terms (the right one, for the sake of definiteness) does not vanish. The normalization condition is imposed on the amplitudes of the geminal expansion (**??**):

$$\langle 0| \, g_m g_m^+ \, |0\rangle = u_m^2 + v_m^2 + 2w_m^2 = 1. \tag{3}$$

The Hamiltonian of the MINDO/3 type is transformed to the HO basis. Also in this case it can be represented as a sum of intraatom (one-center) and interatom (two-center) contributions:

$$\mathbf{H} = \sum_A \mathbf{H}_A + \frac{1}{2} \sum_{A \neq B} \mathbf{H}_{AB}, \tag{4}$$

where the intraatom contribution is:

$$\begin{aligned}
\mathbf{H}_A = & \sum_{t_m \in A} \left(U_m^t - \sum_{B \neq A} \gamma_{AB} Z_B \right) \sum_\sigma t_{m\sigma}^+ t_{m\sigma} - \\
& - \sum_{\substack{t_{m_1} t_{m_2} \in A \\ m_1 < m_2}} \beta^A_{t_{m_1} t'_{m_2}} \sum_\sigma \left(t_{m_1\sigma}^+ t'_{m_2\sigma} + h.c. \right) + \\
& + \tfrac{1}{2} \sum_{\substack{t_{m_1} t'_{m_2}, \\ t''_{m_3} t'''_{m_4} \in A}} \left(t_{m_1} t'_{m_2} \mid t''_{m_3} t'''_{m_4} \right)^A \sum_{\sigma\tau} t_{m_1\sigma}^+ t''^+_{m_3\tau} t'''_{m_4\tau} t'_{m_2\sigma},
\end{aligned} \tag{5}$$

while the interatom contribution is:

$$\begin{aligned}
\mathbf{H}_{AB} = & - \sum_{\substack{t_{m_1} \in A \\ t'_{m_2} \in B}} \beta^{AB}_{m_1 m_2} \sum_\sigma \left(t_{m_1\sigma}^+ t'_{m_2\sigma} + h.c \right) + \\
& + \gamma_{AB} \sum_{\substack{t_{m_1} \in A \\ t'_{m_2} \in B}} \sum_{\sigma\tau} t_{m_1\sigma}^+ t'^+_{m_2\tau} t'_{m_2\tau} t_{m_1\sigma},
\end{aligned} \tag{6}$$

where *h.c.* stands for hermitian conjugation and $|t_m\rangle$ denotes one of the two HO's (right or left) belonging to the m-th geminal. The optimal HO's and the amplitudes (u_m, v_m, and w_m) are determined variationally. The results of our calculations have shown that the accuracy of the APSLG-MINDO/3 method is comparable and somewhat better than the SCF-MINDO/3 method when applied to the heats of formation and equilibrium geometries of organic molecules. The dependence of the calculation time on the size of the system (*i.e.* the number of basis functions) is linear [**?**]. Also the APSLG (but not SCF) approach ensures a correct asympthotic of the wave function under the bond cleavage.

2 Theory

Now we consider a method of deriving vertical ionization potentials for the APSLG-type wave function. In the framework of the APSLG method it is very natural to construct $(N-1)$-electron states by extracting an electron from one of the geminals, conserving the geminals' structures for other bonds and/or lone pairs, similarly to the way the ionized states are constructed for the SCF method [**?**]. At the same time the states obtained by extracting an electron from a geminal are not even approximately the eigenstates of the ion. They do not permit to explain the form of the photoelectron spectra. To obtain the correct eigenstates of the ion we take into account the interaction between these $(N-1)$-electron states. The way for constructing these states is the key point of this paper.

When one electron is extracted from the geminal, the remaining electron can occupy either one of the four spin-orbitals in the case of a geminal representing a usual chemical bond or one of the two spin-orbitals in the case of the geminal representing an electron lone pair. If we assume these spin-orbitals to be $|r_{m\sigma}\rangle$ and $|l_{m\sigma}\rangle$, we obtain configurations strongly interacting due to the large intrabond resonance terms. In this context it is more natural to use so-called bond orbitals (BO's) which constitute an alternative one-electron basis set. The BO's related to a given geminal (bond) are expanded in terms of the corresponding HO's:

$$\left\{ \begin{array}{l} b_{m\sigma} = x_m l_{m\sigma} + y_m r_{m\sigma} \\ a_{m\sigma} = -y_m l_{m\sigma} + x_m r_{m\sigma} \end{array} \right. . \tag{7}$$

These orbitals are also normalized:

$$x_m^2 + y_m^2 = 1 \tag{8}$$

and orthogonal

$$\langle 0|\, a_{m\sigma} b_{m\sigma}^{+} \,|0\rangle = \langle 0|\, b_{m\sigma} a_{m\sigma}^{+} \,|0\rangle = 0. \tag{9}$$

The coefficients x_m and y_m must be determined on the basis of the L-orthogonality condition (*i.e.* the states generated by the action of the BO related fermion operators on the ground state of the molecule in the APSLG approximation are orthogonal):

$$\langle 0| \, g_m a_{m\sigma} b_{m\sigma}^+ g_m^+ \, |0\rangle = \langle 0| \, g_m b_{m\sigma} a_{m\sigma}^+ g_m^+ \, |0\rangle = 0. \tag{10}$$

If we denote the coefficients as $x_m = \cos \varphi_m$ and $y_m = \sin \varphi_m$, then the angle φ_m is determined by expression:

$$\varphi_m = \frac{1}{2} \arctan \left(\frac{2w_m}{v_m - u_m} \right). \tag{11}$$

It should be noted that the orbitals defined by Eq. (**??**) are respectively usual bonding and antibonding orbitals for the m-th bond. The reciprocal transition to the atomic HO's is given by:

$$\begin{cases} r_{m\sigma} = x_m a_{m\sigma} + y_m b_{m\sigma} \\ l_{m\sigma} = x_m b_{m\sigma} - y_m a_{m\sigma} \end{cases}. \tag{12}$$

The geminal of the m-th bond can be rewritten in terms of the bonding and antibonding BO's:

$$g_m^+ = U_m b_{m\alpha}^+ b_{m\beta}^+ + V_m a_{m\alpha}^+ a_{m\beta}^+, \tag{13}$$

where the new coefficients of the geminal expansion comply the following normalization conditions for the geminals:

$$U_m^2 + V_m^2 = 1. \tag{14}$$

Substituting Eq. (**??**) into Eq. (**??**) and comparing the result with Eq. (**??**), we obtain that the coefficients in Eq. (**??**) are

$$\begin{cases} U_m = \frac{1}{2} \left(u_m + v_m + \sqrt{(u_m - v_m)^2 + 4w_m^2} \right), \\ V_m = \frac{1}{2} \left(u_m + v_m - \sqrt{(u_m - v_m)^2 + 4w_m^2} \right). \end{cases} \tag{15}$$

The reverse relation between the amplitudes of the geminal in terms of the atomic HO's and BO's is unique and can be written as

$$\begin{cases} u_m = U_m y_m^2 + V_m x_m^2 \\ v_m = U_m x_m^2 + V_m y_m^2 \\ w_m = (U_m - V_m) \, x_m y_m \end{cases}. \tag{16}$$

The both basis sets (BO's and HO's) will be used hereinafter. It is necessary to mention that in the case of electron lone pair we can construct only one BO which coincides with the HO.

Now we consider a method of constructing the ionized states. After one electron is extracted from a geminal the remaining electron may occupy either the bonding or antibonding BO. All other bonds are represented by their ground state geminals. Thus generated $(N-1)$-electron states are:

$$\left|\Phi_{c_{m\sigma}}^{+}\right\rangle = \left(\prod_{k\neq m} g_k^{+}\right) c_{m\sigma}^{+}\left|0\right\rangle, \tag{17}$$

where the fermion creation operator $c_{m\sigma}^{+}$ stands for either of the fermion operators ($b_{m\sigma}^{+}$ or $a_{m\sigma}^{+}$) creating electrons with the spin projection σ. The Hamiltonian Eq. (**??**) does not contain contributions allowing states Eq. (**??**) with different spin projections to interact. Therefore, the eigenstates of the ion can be presented by a linear combination of the basis functions with the same spin projection:

$$\left|\Psi_{n\sigma}^{+}\right\rangle = \sum_{c_m} \chi_{c_m}^{n}\left|\Phi_{c_{m\sigma}}^{+}\right\rangle. \tag{18}$$

The coefficients $\chi_{c_m}^{n}$ are to be determined by solving the eigenvalue problem:

$$\mathbf{H}\left|\Psi_{n\sigma}^{+}\right\rangle = E_n^{+}\left|\Psi_{n\sigma}^{+}\right\rangle. \tag{19}$$

The vertical ionization potentials must be obtained by subtracting the energy of the ground state of the neutral molecule E_0 taken in the APSLG approximation from the eigenenergies E_n^{+} of the ion. If we replace the Hamiltonian in Eq. (**??**) by the operator $\mathbf{H}-E_0\mathbf{I}$, the corresponding eigenvalue problem gives the eigenstates of the ion and the vertical ionization potentials as its eigenvalues. Analogous method was considered in Ref. [**?**] for the localized wave function of the Hartree-Fock method. Moreover, assuming the transferability the matrix elements of the configuration interaction matrix the simple scheme of evaluating the ionization potentials similar to the Hückel method but with atoms replaced by bonds was constructed.

Now we turn to analysis of the matrix elements of $\mathbf{H}-E_0\mathbf{I}$. First we consider the diagonal elements of the operator $\mathbf{H}-E_0\mathbf{I}$. Let us denote

$$\eta_m^{tc} = \left\langle 0\left|t_{m\sigma}c_{m\sigma}^{+}\right|0\right\rangle. \tag{20}$$

This quantity is the coefficient of the BO $|c_m\rangle$ in the expansion for the HO $|t_m\rangle$ (see Eq. (**??**)). Also if $|t_m\rangle$ is one of the two HO's $|r_m\rangle$ or $|l_m\rangle$ then T_m stands for the atom the orbital $|t_m\rangle$ is centered on (R_m or L_m, respectively). The matrix elements of the one-electron density matrix are [**?**, **?**]:

$$\begin{array}{c} P_m^{tt'} = \langle 0 \left| g_m t_{m\sigma}^+ t'_{m\sigma} g_m^+ \right| 0\rangle \,, \\ P_m^{rr} = u_m^2 + w_m^2, \; P_m^{ll} = v_m^2 + w_m^2, \; P_m^{rl} = P_m^{lr} = (u_m + v_m) w_m. \end{array} \tag{21}$$

The matrix elements of the two-electron density matrix are [**?**, **?**]:

$$\begin{array}{c} \Gamma_m^{tt'} = \left\langle 0 \left| g_m t_{m\sigma}^+ t'^+_{m-\sigma} t'_{m-\sigma} t_{m\sigma} g_m^+ \right| 0 \right\rangle, \\ \Gamma_m^{rr} = u_m^2, \; \Gamma_m^{ll} = v_m^2, \; \Gamma_m^{rl} = \Gamma_m^{lr} = w_m^2. \end{array} \tag{22}$$

Using these notations we obtain:

$$\begin{array}{c} H_{c_m c_m} = \left\langle 0 \left| \left(\prod\limits_{k' \neq m} g_{k'} \right) c_{m\sigma} \left(\mathbf{H} - E_0 \mathbf{I} \right) c_{m\sigma}^+ \left(\prod\limits_{k \neq m} g_k^+ \right) \right| 0 \right\rangle = \\ = \sum\limits_{t \in \{r,l\}} \{ (U_m^t - \sum\limits_{B \neq T_m} \gamma_{T_m B} Z_B)[(\eta_m^{tc})^2 - 2P_m^{tt}] - (t_m t_m \mid t_m t_m)^{T_m} \Gamma_m^{tt} \} - \\ -2\beta_{r_m l_m}^{R_m L_m} (\eta_m^{rc} \eta_m^{lc} - 2P_m^{rl}) - 2\gamma_{R_m L_m} \Gamma_m^{rl} + \\ + \sum\limits_{t \in \{r,l\}} [(\eta_m^{tc})^2 - 2P_m^{tt}] \sum\limits_{\substack{t'_q \in T_m \\ q \neq m}} [2(t_m t_m \mid t'_q t'_q)^{T_m} - (t_m t'_q \mid t_m t'_q)^{T_m}] P_q^{t't'} + \\ +2 \sum\limits_{t \in \{r,l\}} [(\eta_m^{tc})^2 - 2P_m^{tt}] \sum\limits_{B \neq T_m} \gamma_{B T_m} \sum\limits_{\substack{t'_q \in B \\ q \neq m}} P_q^{t't'}. \end{array} \tag{23}$$

The off-diagonal matrix elements can be also divided in two classes: (i) those between the ionized states with an electron extracted from one geminal but from the different BO's assigned to the latter; and (ii) those between two ionized states with an electron extracted from two different geminals. Let us consider the first case. Let us set:

$$\overline{c}_{m\sigma} = \left\{ \begin{array}{l} a_{m\sigma}, \text{ if } c_{m\sigma} = b_{m\sigma} \\ b_{m\sigma}, \text{ if } c_{m\sigma} = a_{m\sigma} \end{array} \right. . \tag{24}$$

Then

$$
\begin{aligned}
H_{c_m\overline{c}_m} &= \left\langle 0 \left| \left(\prod_{k'\neq m} g_{k'} \right) c_{m\sigma} \left(\mathbf{H} - E_0 \mathbf{I} \right) \overline{c}^{+}_{m\sigma} \left(\prod_{k\neq m} g^{+}_{k} \right) \right| 0 \right\rangle = \\
&= \sum_{t\in\{r,l\}} (U^t_m - \sum_{B\neq T_m} \gamma_{T_m B} Z_B) \eta^{tc}_m \eta^{t\overline{c}}_m - \beta^{R_m L_m}_{r_m l_m} (\eta^{rc}_m \eta^{l\overline{c}}_m + \eta^{r\overline{c}}_m \eta^{lc}_m) + \\
&+ \sum_{t\in\{r,l\}} \eta^{tc}_m \eta^{t\overline{c}}_m \sum_{\substack{t'_q\in T_m \\ q\neq m}} [2(t_m t_m \mid t'_q t'_q)^{T_m} - (t_m t'_q \mid t_m t'_q)^{T_m}] P^{t't'}_q + \\
&\qquad +2 \sum_{t\in\{r,l\}} \eta^{tc}_m \eta^{t\overline{c}}_m \sum_{B\neq T_m} \gamma_{BT_m} \sum_{\substack{t'_q\in B \\ q\neq m}} P^{t't'}_q .
\end{aligned}
\tag{25}
$$

Let us denote

$$
C_{mc} = \begin{cases} U_m, & \text{if } c_{m\sigma} = b_{m\sigma} \\ V_m, & \text{if } c_{m\sigma} = a_{m\sigma} \end{cases} .
\tag{26}
$$

The off-diagonal matrix element of the Hamiltonian between the ionized states obtained by the electron extraction from the different geminals can be written as

$$
\begin{aligned}
H_{c_m c'_n} &= \left\langle 0 \left| \left(\prod_{k'\neq m} g_{k'} \right) c_{m\sigma} \left(\mathbf{H} - E_0 \mathbf{I} \right) c'^{+}_{n\sigma} \left(\prod_{k\neq n} g^{+}_{k} \right) \right| 0 \right\rangle = \\
&= \sum_{tt'\in\{r,l\}} C_{mc} C_{nc'} \eta^{tc}_m \eta^{t'c'}_n \times \\
&\times \{ \beta^{T_m T'_n}_{t_m t'_n} - \delta_{T_m T'_n} \sum_{\substack{t''_q\in T_m \\ q\neq m,n}} P^{t''t''}_q [2(t''_q t''_q \mid t_m t'_n)^{T_m} - (t''_q t_m \mid t''_q t'_n)^{T_m}] \} - \\
&- \sum_{tt'\in\{r,l\}} \delta_{T_m T'_n} \eta^{tc}_m \eta^{t'c'}_n (t_m t_m \mid t_m t'_n)^{T_m} C_{nc'} [(\eta^{ta}_m)^2 C_{ma} + (\eta^{tb}_m)^2 C_{mb}] - \\
&- \sum_{tt'\in\{r,l\}} \delta_{T_m T'_n} \eta^{tc}_m \eta^{t'c'}_n (t'_n t'_n \mid t'_n t_m)^{T_m} C_{mc} [(\eta^{t'a}_n)^2 C_{na} + (\eta^{t'b}_n)^2 C_{nb}].
\end{aligned}
\tag{27}
$$

In the case of lone pairs these formulae remain true but we must consider only the states of the type $\left|\Phi^{+}_{c_{m\sigma}}\right\rangle$ and the contributions from the "right-end" atom. Due to the spin projection conservation rules, the overall dimension of the matrix to be diagonalized is $2M+N$, where M is the number of chemical bonds and N is the number of electron lone pairs in the molecule.

Another (more sophisticated) possibility to obtain the vertical ionization potentials and the corresponding eigenstates is to allow the non-ionized geminals to relax to accommodate the hole. Such a procedure must be performed separately for each many-electron basis state. The whole procedure leads to the basis states analogous to Eq. (**??**) but with the geminals which are not taken from the ground state of the neutral molecule but are obtained with use of an optimization procedure for $(M+N-1)$ geminals in the system with an electron extracted from one of geminals of the molecule under consideration. In a molecule with a hole the effective Hamiltonians for each geminal differ from those in the neutral molecule. Thus the optimal geminals for the ionized molecule differ from those in the neutral molecule as well.

The abovementioned adjustment of the geminals to the presence of the hole is nothing else but polarization of these geminals in the Coulomb field induced by the hole. The polarization of the SCF localized wave function by the hole was investigated in the Ref. [?] in the second order of the perturbation theory. Let us consider a method which takes into account the polarization of the geminals in the presence of a hole. For this end we construct the effective Hamiltonians for each of the geminals in the field of other geminals including that where the hole is residing. The effective Hamiltonian for the k-th geminal in the field of other geminals and of an electron located on the bond spin-orbital $|c_{m\tau}\rangle$ of the m-th (ionized) bond $(k \neq m)$ can be presented as:

$$H^{eff}_{kc_{m\tau}} = H^{core}_{kc_{m\tau}} + H^{1,intra}_{kc_{m\tau}} + H^{1,inter}_{kc_{m\tau}} + H^{res}_{kc_{m\tau}} + H^{2,intra}_{kc_{m\tau}} + H^{2,inter}_{kc_{m\tau}}, \tag{28}$$

where the contributions have the following meaning: the first term describes the attraction of electrons to the cores:

$$H^{core}_{kc_{m\tau}} = \sum_{t\in\{r,l\}} (U^t_k - \sum_{B\neq T_k} \gamma_{T_k B} Z_B) \sum_\sigma t^+_{k\sigma} t_{k\sigma}. \tag{29}$$

One-center repulsion of electrons of one bond gives the contribution into the Hamiltonian:

$$H^{1,intra}_{kc_{m\tau}} = \sum_{t\in\{r,l\}} (t_k t_k \mid t_k t_k)^{T_k} t^+_{k\alpha} t^+_{k\beta} t_{k\beta} t_{k\alpha}, \tag{30}$$

and the one-center contribution from repulsion of the electrons of the k-th bond from the electrons of other bonds can be written as

$$\begin{aligned} H^{1,inter}_{kc_{m\tau}} = &\sum_{t\in\{r,l\}} \sum_{\substack{t'_q\in T_k \\ q\neq k,m}} [2(t_k t_k \mid t'_q t'_q)^{T_k} - (t_k t'_q \mid t_k t'_q)^{T_k}] P^{t't'}_q \sum_\sigma t^+_{k\sigma} t_{k\sigma} + \\ + &\sum_{tt'\in\{r,l\}} \delta_{T_k T'_m} (\eta^{t'c}_m)^2 [(t_k t_k \mid t'_m t'_m)^{T_k} \sum_\sigma t^+_{k\sigma} t_{k\sigma} - (t_k t'_m \mid t_k t'_m)^{T_k} t^+_{k\tau} t_{k\tau}]. \end{aligned} \tag{31}$$

The contribution from the intrabond resonance has the form:

$$H^{res}_{kc_{m\tau}} = -\beta^{R_k L_k}_{r_k l_k} \sum_\sigma \left(r^+_{k\sigma} l_{k\sigma} + l^+_{k\sigma} r_{k\sigma} \right). \tag{32}$$

The contribution from the Coulomb repulsion between electrons located on the different atoms also can be divided into the intrabond

$$H^{2,intra}_{kc_{m\tau}} = \gamma_{R_k L_k} \sum_{\sigma} r^{+}_{k\sigma} l^{+}_{k-\sigma} l_{k-\sigma} r_{k\sigma} \tag{33}$$

and the interbond

$$\begin{aligned} H^{2,inter}_{kc_{m\tau}} = \sum_{t\in\{r,l\}} \sum_{B\neq T_k} \gamma_{T_k B} \times \\ \times \sum_{\substack{t'_q \in B \\ q\neq k}} [\delta_{qm} (\eta^{t'c}_{m})^2 + 2(1-\delta_{qm}) P^{t't'}_{q}] \sum_{\sigma} t^{+}_{k\sigma} t_{k\sigma}. \end{aligned} \tag{34}$$

contributions. The contributions of Eqs. (**??**) and (**??**) to the effective Hamiltonian are responsible for the polarization. The polarized geminals can be obtained by solving the eigenvalue problem

$$H^{eff}_{kc_{m\tau}} \widetilde{g}_{kc_{m\tau}} = \widetilde{\epsilon}_{kc_{m\tau}} \widetilde{g}_{kc_{m\tau}}, \tag{35}$$

where $\widetilde{g}_{kc_{m\tau}}$ is the k-th geminal polarized by the hole on the m-th geminal with remaining electron residing on the bond spin orbital $|c_{m\tau}\rangle$. The expressions for the matrix elements of the operator $\mathbf{H} - E_0\mathbf{I}$ in the basis of the ionized basis states with the adjusted (polarized) geminals are very cumbersome and will not be presented here. The main difference between the off-diagonal matrix elements of two methods can be termed as multiplication by the factors similar to the product of the overlap integrals between the geminals $\widetilde{g}_{kc_{m\tau}}$ with different values of k. The diagonal matrix elements are shifted due to changes in the contributions to the Hamiltonian from the non-ionized geminals caused by their polarization.

3 Results and Discussion

We have implemented two above mentioned computational procedures which determine the vertical ionization potentials. The APSLG-MINDO/3 approximation [**?**, **?**] has been employed for calculation of the ground states of these molecules and for parameterizing the Hamiltonian matrices for the ionized states. The specific structure of the APSLG approximation restricts these schemes only to the molecules which can be represented by structures with well defined separate chemical bonds. First we compare both procedures with the results of the SCF-MINDO/3 method for a series of normal hydrocarbons. The higher members of this series simulate the polyethylene chain. The first question in this context concerns the structure of the hole in the higher hydrocarbons: whether it is localized on several chain segments or delocalized over the whole chain? The one-electron approximation results in the plane-wave like structure for the wave function of the lowest ionized state (ground state of the cation), *i.e.* the coefficient of the k-th orbital on the n-th atom in the hydrocarbon molecule $C_N H_{2N+2}$ is:

$$c_{nk} = \sqrt{\frac{2}{N+1}} \sin \frac{\pi k n}{N+1}. \tag{36}$$

(In this model one orbital per methyl or methylene group in the chain is assumed). At the same time the variation of the lengths of chemical bonds in this simplest model yields the localized ionized state [**?**]. In the context of our model the following question worths to be studied: does the method operating with local entities like geminals yield localized or delocalized description of a hole? Another question to be studied for a series of hydrocarbons is the dependence of the vertical ionization potential on the hydrocarbon chain length.

These dependencies obtained by the SCF-MINDO/3 method, the APSLG-MINDO/3 method without polarization of the geminals and the APSLG-MINDO/3 method which takes into account the polarization of geminals in the presence of the hole are given in Table 1. The geometry structures of the neutral molecules in all these cases were obtained by minimizing the energy of the molecule in its ground state by the respective method (SCF-MINDO/3 or APSLG-MINDO/3). Fig. 1 represents all these three dependencies as compared with the data of photoelectron spectroscopy. The analysis of these data reveals that both the APSLG-based methods described in the previous section give the values of the vertical ionization potentials which are lower than the SCF method does. As one can expect the vertical ionization potentials obtained by the APSLG-MINDO/3 method with the polarized geminals are always lower than those obtained by the APSLG-MINDO/3 method with the fixed geminals. This is due to a larger number of degrees of freedom in the case of the polarized geminals. The numerical values of the vertical ionization potential obtained by the APSLG-MINDO/3 based method with fixed geminals are in a good agreement with the experimental data. It is necessary to mention that the experimental data on the ionization potentials are very divergent (see, for example, Refs. [?, ?, ?] for methane and Refs. [?, ?, ?, ?] for ethane and propane). At the same time the values of the vertical ionization potential obtained by the APSLG-MINDO/3 based method with polarized geminals are noticeably (by more than 0.5 eV) lower. So, the photoionization experiment for the $C_{11}H_{24}$ molecule [?] gives the value of the first adiabatic ionization potential equal to 9.6 eV. The APSLG-MINDO/3 based method with the polarized geminals gives even the value of the vertical ionization potential by 0.4 eV lower than the experimental adiabatic one. It can be readily understood when we compare the ways of obtaining the ground state energy for neutral molecules and their positive ions. The wave function of the ion with fixed geminals has approximately the same level of correlation as the wave function of the neutral molecule. At the same time in the case of the APSLG-based method with polarized geminals this balance is broken.

Next we considered the width of the valence band in polyethylene. To study this topic we assume that the bandwidth in polyethylene is close to that in the hydrocarbon $C_{20}H_{42}$. In the case of the SCF-MINDO/3 method this bandwidth is the energy difference between the highest and lowest occupied molecular orbitals. It equals to 26.9 eV. The APSLG method gives another definition for the width of the valence band. We define it as a difference between energies of two ionized states — one with number equal to the number of geminals and another which is the lowest on the energy scale. This definition coincides with the usual one when applied to the SCF wave function. In the case of the both APSLG-MINDO/3 based methods we obtain the width of the valence band to be 18.8 eV that is significantly lower than the SCF value.

Close to this question is that about reproducing the positions of the peaks in the photoelectron spectrum. For example, in the case of methane the experimental data give the second peak in the photoelectron spectrum at about 23 eV [?]. The SCF-MINDO/3 method gives 27 eV for this quantity. The APSLG-MINDO/3 method with the fixed geminals gives 26.3 eV (the polarization of geminals lowers this value by 0.1 eV only). Thus, both semiempirical quantum chemical methods push this value essentially higher than the experimental. In the case of highly symmetric molecules their photoionization yields degenerate ionized states. For example, in the case of methane the triply degenerate peak near 13 eV is observed. In the case of ethane the doubly degenerate peak near 11.5 eV is observed. These experimental data are explained theoretically on the basis of the orbital theories (see, for example, [**?**, **?**]). The origin of these peaks is ascribed to extraction of an electron from the higher triply degenerate molecular orbital in the case of methane (the T_2 representation of the T_d point group, which is the symmetry group of the Fock operator for the methane molecule) and from the doubly degenerate molecular orbital in the case of ethane. This fact for years served as an argument in favor of the orbital picture of the electronic structure of a molecule although in fact it is a consequence of the SCF approximation. Therefore it was interesting to consider the capacity of the APSLG approximation to reproduce correctly the form of photoelectron spectra. In the framework of the above scheme we have studied the degeneracy of the ionized states for the methane and ethane molecules. It turned out that the experimental structure of the spectrum is reproduced by our calculations. Of course, it is totally controlled by the symmetry of configuration interaction matrix. In the case of methane the Hamiltonian matrix consists of four equal diagonal 2×2 blocks. The off-diagonal 2×2 blocks are also equal. It leads to the spectrum with two triply degenerated and two non-degenerated eigenvalues.

Another question to be studied is the localization of the hole in polyethylene (or in our case, in higher hydrocarbons). The eigenfunction of an ion can be obtained from the wave function of the ground state of the molecule by acting with an electron annihilating operator:

$$\left|\Psi^{+}_{n\sigma}\right\rangle = \mathbf{A}_{n\sigma}\left|\Psi_0\right\rangle . \tag{37}$$

In the case of the SCF-based approach leading to the Koopmans' theorem the operator $\mathbf{A}_{n\sigma}$ is the operator annihilating an electron on one of the molecular orbitals. To represent the hole in the case of the correlated (APSLG) ground state the concept of the Dyson orbitals [**?**] can be used. These orbitals in a most general form are defined by the expression:

$$g_{n\sigma}(x) = \left\langle \Psi^{+}_{n\sigma}\left|\psi(x)\right|\Psi_0\right\rangle , \tag{38}$$

where the $\psi(x)$ is the fermion field operator annihilating an electron in the point with the coordinates $x = (\mathbf{r}, \tau)$ (where τ stands for the spin projection of the annihilated electron). In the AO (or LCAO) representation the Dyson orbitals are expressed as linear combinations of the respective basis functions. In the case of the SCF approach Dyson orbitals coincide with molecular orbitals, and, therefore $|g_{n\sigma}\rangle = \mathbf{A}_{n\sigma}^{+}|0\rangle$. Within the APSLG-based scheme with the fixed geminals the operators $\mathbf{A}_{n\sigma}$ are defined by the expression

$$\mathbf{A}_{n\sigma} = \sum_m \left(\frac{\chi_{b_m}^n}{U_m} b_{m\sigma} + \frac{\chi_{a_m}^n}{V_m} a_{m\sigma} \right), \tag{39}$$

while the Dyson orbitals are

$$|g_{n\sigma}\rangle = \sum_m \left(\chi_{b_m}^n U_m |b_{m\sigma}\rangle + \chi_{a_m}^n V_m |a_{m\sigma}\rangle \right). \tag{40}$$

Therefore, one-electron functions $\mathbf{A}_{n\sigma}^{+}|0\rangle$ and $|g_{n\sigma}\rangle$ do not coincide. Moreover, these functions are not normalized. At the same time one can check that $\langle 0 | A_{n\sigma} | g_{m\tau}\rangle = \delta_{mn}\delta_{\sigma\tau}$ which serves as the biorthonormalization condition for the Dison orbitals and the hole creation (electron annihilation) operators.

In the case of the APSLG approach with polarized geminals the one-electron operators $\mathbf{A}_{n\sigma}$ can not be easily determined. Therefore, to compare the localization of a hole for two APSLG-based methods we use the concept of Dyson orbitals. In higher hydrocarbons the Dyson orbitals obtained within the both computational schemes, which correspond to the lowest first ionization potential are delocalized over the chain and are largely located on the C-C bond backbone. This result coincides with that of Ref. [**?**]. In the case of the APSLG-based methods the Dyson orbital is slightly more localized than in the case of the SCF method but also has the sine-like form with the maximum at the center of the chain. The Dyson orbitals of the two APSLG-based methods are similar as well, but the charge distributions in the alkane cations in these two schemes differ noticeably. In the case of the APSLG-MINDO/3 method with the fixed geminals the charges on the hydrogen atoms are very close to those in the neutral molecule while in the case of the APSLG-MINDO/3 method with the polarized geminals the charges on the hydrogen atoms became essentially — by 0.035 of unit charge (for hydrogens connected to the carbon atoms near the center of the chain) — more positive than in the neutral molecule, due to electron redistribution in the C-H bonds which are not affected by the ionization directly.

Let us consider ionization of molecules of other classes of compounds. In Table 2 some results of the calculation on the first vertical ionization potentials by the APSLG-based method with fixed geminals in comparison with the experimental data are presented for some simple molecules. The analysis of the data of Table 2 shows that the APSLG-MINDO/3 based method with fixed geminals gives the values of the first vertical ionization potential which are close to the experimental ones for all the studied molecules except cyclopropane.

The analysis of the wave function of the ionized state in the case of the ammonia or water molecules has shown that the main contribution to the hole is given by the electron lone pairs (73.1% in the case of ammonia and 99.9% in the case of water). It can also be noticed that the ionization potentials of normal saturated hydrocarbons are essentially higher than those of their cyclic analogues with the same number of carbon atoms in agreement with experimental data.

The ionization potentials of methylamin and ethylamin are very close. This is due to the local character (lone pair) of the first vertical ionized state. This state is only slightly sensitive to the changes taking place far from the lone pair (the transition from the methylamin to ethylamin lowers the calculated first vertical ionization potential by less than 0.05 eV, the experimental change is also small). The changes in the local surrounding of the nitrogen atom such as the transition from ammonia to methylamin or from methylamin to dimethylamin stronger affects the first vertical ionization potential (by 1.4 eV in the first case) in accordance with the experimental data. It can be noticed that the alkyl substituents at the nitrogen atom increase the stability (lower the energy) of the first ionized state. This fact can be explained by taking into account the importance of configuration with ionized lone electron pair for this ionized state and the accepted in the organic chemistry electron-donating character of alkyl groups (the matrix element of the Hamiltonian between the ionized states where the remaining electron resides in the HO of the lone pair and that with remaining electron on the bonding orbital of the N-H bond are -3.92 eV for ammonia and -3.56 eV for methylamine). The addition of alkyl groups to oxygen atom of the water molecule decreases the first vertical ionization potential as well. The first vertical ionization potentials in the oxygen-containing molecules are as well sensitive to the kind and number of alkyl substituents at the heteroatom (see Table 2).

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Table 1: The first vertical ionization potentials (in eV) in a series of hydrocarbons from CH_4 to $C_{20}H_{42}$ obtained by the SCF-MINDO/3 and by the both APLSG-based procedures.

N	**SCF**	**fixed geminals**	**polarized geminals**
1	13.289	13.306	13.079
2	11.758	11.657	11.212
3	11.291	11.130	10.572
4	11.044	10.862	10.266
5	10.916	10.600	10.034
6	10.722	10.383	9.789
7	10.606	10.226	9.612
8	10.514	10.107	9.476
9	10.424	10.015	9.371
10	10.368	9.942	9.288
11	10.328	9.885	9.222
12	10.279	9.838	9.169
13	10.232	9.800	9.125
14	10.220	9.768	9.089
15	10.192	9.742	9.059
16	10.172	9.720	9.034
17	10.151	9.701	9.012
18	10.136	9.685	8.994
19	10.108	9.671	8.978
20	10.105	9.658	8.964

Table 2: The first vertical ionization potentials (eV) for some simple molecules obtained by the APSLG-based method with fixed geminals.

Molecule	**Calculated value, eV**	**Experimental value, eV**
H_2	15.614	15.43 [?]
cyclopropane	10.058	11.0 [?]
C_2H_4	10.418	10.51 [?]
NH_3	10.117	10.15 [?]
N_2H_4	8.856	8.74 [?]
CH_3NH_2	8.741	8.97 [?]
$C_2H_5NH_2$	8.789	8.66 [?]
H_2O	12.794	12.62 [?]
CH_3OH	10.781	10.84 [?]
C_2H_5OH	10.470	10.47 [?]